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# HOWARD LUCAS

1885—1963

A Biographical Memoir by WILLIAM G. YOUNG AND SAUL WINSTEIN

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Biographical Memoir

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# HOWARD JOHNSON LUCAS

March 7, 1885-June 22, 1963

# BY WILLIAM G. YOUNG AND SAUL WINSTEIN

Howard J. Lucas was born to William W. Lucas and Marian Curtis Lucas in Marietta, Ohio, on March 7, 1885. He attended Ohio State University for both undergraduate and graduate work, receiving the B.S. degree in 1907 and the M.A. degree in 1908. Many years later, in 1953, he was awarded an Honorary D.Sc. degree by that institution. He became a Fellow in chemistry at the University of Chicago in 1909-1910, working toward a Ph.D. degree. At this point he was forced to leave school, owing to the death of his father, and he became Assistant Chemist in the U.S. Department of Agriculture (1910-1913). From 1913 to 1915 he served as Instructor at Throop College of Technology (which later became the California Institute of Technology). He was promoted to Associate Professor of Organic Chemistry in 1915 and to Professor in 1940. He served as Visiting Professor of the University of Hawaii in 1953 and Visiting Professor at Ohio State University in 1954-1955. Although he became Emeritus Professor of Organic Chemistry at the California Institute of Technology in 1955, he continued actively in research until shortly before his death.

Lucas was interested in the profession of chemistry from the time he joined the American Chemical Society in 1909. He became active in the Southern California section of the society about 1916, serving on many committees until he became chairman of the section in 1931-1932. He helped promote an unusual high school chemistry contest, which is still an important activity of the section today.

Professor Lucas was honored by election to the National Academy of Sciences in 1957, after having been the second recipient of the American Chemical Society's award in Chemical Education, sponsored by the Scientific Apparatus Makers Association in 1953. The purpose of this award is to recognize outstanding contributions to chemical education. These recognitions came late in his career, primarily because his education was interrupted by the death of his father and because he joined the California Institute of Technology while it was in its infancy. He spent the better part of ten years working with several other talented people developing a curriculum which was based on extremely high standards and close working relationships between professor and student. As Cal Tech progressed, so did Lucas's opportunities to secure graduate students of high calibre. Although he was the only organic chemist on the staff in the early days, his influence and inspiration in his particular field caused many talented students to choose organic chemistry, despite the great attractiveness of the field of physical chemistry, at that time under Arthur A. Noyes.

Lucas's outstanding skills as an educator were devoted to bringing out the best efforts inherent in the individual as a student and a researcher in the field. His example of doing research himself, particularly in cooperation with his students in those fields of organic chemistry which could take advantage of the skills usually associated with physical chemistry, produced talented men who continued laying the foundation of what is now known as physical organic chemistry. All of the men who were associated with him as students

considered him to be an excellent teacher. He gave one the feeling that he was sincerely interested in imparting knowledge and developing the student's laboratory skill. However, to quote one of Lucas's most successful students, "One needed to serve as a teaching assistant to obtain a real insight into Lucas, the teacher." All were amazed at the care that went into setting up and testing lecture demonstrations. The underlying principle of Professor Lucas's teaching method was to "get the student to think" and to "conduct experiments with the utmost accuracy and with carefully purified chemicals."

In trying to get the student to think, Professor Lucas emphasized the physical chemical side of organic chemistry. In so doing he did much to simplify organic chemistry for the student, tying it in with the chemistry the student already knew, especially at Cal Tech. Since there was no text available for this approach, Lucas wrote his own text, Organic Chemistry, which became a classic in the field. This book was one of the first to recognize the value of electronic interpretations in the field of organic chemistry, clearly relating organic chemistry to modern chemical theory.

The research program carried forward by Professor Lucas provided a substantial fraction of the theoretical basis of present-day organic chemistry. He did some of the very first research in physical organic chemistry.

When H. J. Lucas began his research, the electron-pair description of the covalent bond had just been recognized; he made the first clear application of the idea of electron displacement in molecules to the interpretation of the behavior of organic substances. He correlated the direction of addition of unsymmetrical reagents to olefins and other properties of molecules, such as acid strength, with relative electronegativities of substituent groups. He made a start on the more complex problem of electron displacement in aromatic

substances and contributed to the understanding of aromatic substitution. His contributions and ideas were incorporated in the comprehensive electronic theory of organic reactions later developed mainly by the English.

Much of Professor Lucas's work involved unsaturated compounds. He and his students prepared pure cis- and trans-2-butenes and 2-pentenes. They carried out a comprehensive series of investigations which elucidated the kinetics and mechanisms of hydration of olefinic and acetylenic materials. Lucas's interest in the interpretation of the behavior of  $\pi$ -electron-containing materials led him to a study of the ability of olefins to complex with acceptor species such as silver ion and mercuric ion. This work and its interpretation anticipated by some ten years the more recent general concept of " $\pi$ -complexes."

A good deal of Lucas's work dealt with the stereochemistry of materials with two asymmetric centers, such as glycols, epoxides, aminoalcohols, and dihalides, and the stereochemistry of their reactions. The work on substitution reactions of such materials led to the now generally recognized participation of neighboring functional groups in substitution reactions by way of cyclic intermediates such as ethylene bromonium and chloronium ions.

An interesting sideline carried along by Professor Lucas was qualitative organic analysis. Besides teaching this subject in an extremely fundamental manner, he made occasional original contributions to the field. For example, his hydrochloric acid-zinc chloride reagent for differentiation of primary, secondary, and tertiary alcohols is commonly known among organic chemists as the "Lucas reagent."

Professor Lucas died June 22, 1963, in Pasadena, California. He had been in poor health for some time because of a heart ailment.

# **BIBLIOGRAPHY**

#### KEY TO ABBREVIATIONS

Ind. Eng. Chem., Anal. Ed. = Industrial and Engineering Chemistry, Analytical Edition

Ind. Eng. Chem. = Industrial and Engineering Chemistry (formerly Journal of Industrial and Engineering Chemistry)

J. Am. Chem. Soc. = Journal of the American Chemical Society

Org. Syn. = Organic Syntheses

#### 1909

With W. McPherson. The action of unsymmetrical benzoylphenylhydrazine on orthobenzoquinone. J. Am. Chem. Soc., 31:281-84.

#### 1913

The determination of nitrobenzene in peanut oil. J. Ind. Eng. Chem., 5:576-77.

#### 1914

With R. del Valle Sárraga and J. Roman Benitez. A study of the milk of Puerto Rican cows. J. Ind. Eng. Chem., 6:22-24.

#### 1917

With A. R. Kemp. The determination of silver in organic compounds. J. Am. Chem. Soc., 39:2074-78.

#### 1921

With A. R. Kemp. Chromo-isomeric silver salts of pentabromophenol and a theory of chromo-isomerism of solid compounds. J. Am. Chem. Soc., 43:1654-65.

#### 1924

With A. Y. Jameson. Electron displacement in aliphatic compounds. I. Electron displacement versus alternate polarity in carbon compounds. J. Am. Chem. Soc., 46:2475-82.

- With Hollis W. Moyse. Electron displacement in carbon compounds. II. Hydrogen bromide and 2-pentene. J. Am. Chem. Soc., 47:1459-61.
- With Thomas P. Simpson and James M. Carter. Electron displacement in carbon compounds. III. Polarity differences in carbon-hydrogen unions. J. Am. Chem. Soc., 47:1462-69.

#### 1926

Electron displacement in carbon compounds. IV. Derivatives of benzene. J. Am. Chem. Soc., 48:1827-38.

# 1927

- With Murray N. Schultz. The sulfonation of *ortho*-toluidine and the preparation of sodium 6-chloro-5-nitro-*meta*-toluenesulfonate. J. Am. Chem. Soc., 49:298-302.
- With Fred J. Ewing. A new method of preparing phosphorus pentafluoride. J. Am. Chem. Soc., 49:1270.
- An all glass distilling tube without constriction. Ind. Eng. Chem., 19:680.

#### 1928

- With Nathan F. Scudder. The preparation of 2-bromo-p-cresol from p-nitrotoluene. J. Am. Chem. Soc., 50:244-49.
- With John Buxton. The analysis of brominated cresols. J. Am. Chem. Soc., 50:249-52.
- With Robert T. Dillon. The synthesis of 1-butene. J. Am. Chem. Soc., 50:1460-69.
- With Robert T. Dillon. Some derivatives of *n*-heptane. J. Am. Chem. Soc., 50:1711-14.

- Electron displacement in carbon compounds. V. The addition of hydrogen chloride to 3-ethyl-2-pentene. J. Am. Chem. Soc., 51:248-53.
- With Carlisle H. Bibb. Air oxidation of hydrocarbons catalyzed by nitrogen oxides. I. Natural gas. Ind. Eng. Chem., 21:633-35.

- With Carlisle H. Bibb. Air oxidation of hydrocarbons catalyzed by nitrogen oxides. II. Benzene. Ind. Eng. Chem., 21:635-39.
- With William G. Young and Robert Dillon. The synthesis of the isomeric 2-butenes. J. Am. Chem. Soc., 51:2528-34.
- With William G. Young. Condensation of acetaldehyde with methylmalonic ester. Methylations with methyl bromide. J. Am. Chem. Soc., 51:2535-38.
- With Edgar P. Valby. The ionization constant of para-cyanobenzoic acid. J. Am. Chem. Soc., 51:2718-20.

- With H. Darwin Kirschman and Baker Wingfield. A comparison method for determining ionization constants with a quinhydrone reference electrode. J. Am. Chem. Soc., 52:23-28.
- A new test for distinguishing the primary, secondary, and tertiary saturated alcohols. J. Am. Chem. Soc., 52:802-4.
- With Robert T. Dillon and William G. Young. Qualitative estimation of the composition of butene mixtures by distillation methods. J. Am. Chem. Soc., 52:1949-53.
- With Robert T. Dillon and William G. Young. The reaction rates of potassium iodide with 1,2- and 2,3-dibromobutane; the analysis of mixtures of the normal butenes. J. Am. Chem. Soc., 52:1953-64.
- With William G. Young. The composition of butene mixtures resulting from the catalytic decomposition of the normal butyl alcohols. J. Am. Chem. Soc., 52:1964-70.

#### 1933

With Yun-pu Liu. The nitration of p-cresol and of p-cresyl carbonate in the presence of sulfuric acid. J. Am. Chem. Soc., 55:1271-80.

- With W. F. Eberz. The hydration of unsaturated compounds. I. The hydration rate of isobutene in dilute nitric acid. J. Am. Chem. Soc., 56:460-64.
- With W. F. Eberz. The hydration of unsaturated compounds. II. Equilibrium between isobutene and tert-butanol and the free

- energy of hydration of isobutene. J. Am. Chem. Soc., 56:1230-34.
- With Yun-pu Liu. The hydration of unsaturated compounds. III. The hydration rate of trimethylethylene in aqueous solutions of acids. J. Am. Chem. Soc., 56:2138-40.

- With A. N. Prater and R. E. Morris. The reaction between oxygen and 2-butene. J. Am. Chem. Soc., 57:723-27.
- Organic Chemistry. New York, American Book Company. vi + 686 pp.

#### 1936

- With E. R. Kennedy and C. A. Wilmot. The decomposition of di-ortho-tolyliodonium iodide. J. Am. Chem. Soc., 58:157-60.
- With C. E. Wilson. Stereochemical relationships of the isomeric 2,3- butanediols and related compounds; evidence of Walden inversion. J. Am. Chem. Soc., 58:2396-2402.

- With W. F. Eberz, H. Welge, and D. M. Yost. The hydration of unsaturated compounds. IV. The rate of hydration of isobutene in the presence of silver ion. The nature of the isobutene-silver complex. J. Am. Chem. Soc., 59:45-49.
- With R. H. Frieman and E. R. Kennedy. The hydration of unsaturated compounds. V. The rate of hydration of acetylene in aqueous solution of sulfuric acid and mercuric sulfate. J. Am. Chem. Soc., 59:722-26.
- With S. Winstein. The hydration of unsaturated compounds. VI. The rate of hydration of trans-crotonaldehyde. The equilibrium between trans-crotonaldehyde and aldol in dilute aqueous solution. J. Am. Chem. Soc., 59:146-65.
- With A. N. Prater. The isomeric 2-pentenes. J. Am. Chem. Soc., 59:1682-86.

With C. E. Redemann. The rapid saponification of esters by potassium hydroxide in diethylene glycol. An aid in identification and analysis. Ind. Eng. Chem., Anal. Ed., 9:521-22.

#### 1938

- With David Pressman. The determination of unsaturation in organic compounds by means of the mercury-catalyzed reaction with standard bromate-bromide solution. Ind. Eng. Chem., Anal. Ed., 10:140-42.
- With S. Winstein. The coordination of silver ion with unsaturated compounds. J. Am. Chem. Soc., 60:836-48.

# 1939

- With S. Winstein. Retention of configuration in the reaction of 3-bromo-2-butanols with hydrogen bromide. J. Am. Chem. Soc., 61:1576-80.
- With S. Winstein. The reaction steps in the conversion of 2,3-diacetoxybutane to 2,3-dibromobutane. J. Am. Chem. Soc., 61:1581-84.
- With D. Pressman. The hydration of unsaturated compounds. VII. The rate of hydration of crotonic acid; the rate of dehydration of beta-hydroxybutyric acid; the equilibrium between crotonic acid and beta-hydroxybutyric acid in dilute aqueous solution. J. Am. Chem. Soc., 61:2271.
- With S. Winstein. The loss of optical activity in the reaction of the optically active *erythro* and *threo*-3-bromo-2-butanols with hydrobromic acid. J. Am. Chem. Soc., 61:2845-48.
- With F. R. Hepner and S. Winstein. The coördination complexes of mercuric ion with cyclohexene. J. Am. Chem. Soc., 61.3102-6.
- With C. E. Redemann. Ionization constants and hydrolytic degradations of cyameluric and hydromelonic acids. J. Am. Chem. Soc., 61:3420-24.

#### 1940

With C. E. Redemann. Some derivatives of cyameluric acid and probable structures of melam, melem, and melon. J. Am. Chem. Soc., 62:842-46.

- With W. T. Stewart. Esters of alginic acid. J. Am. Chem. Soc., 62:1070-74.
- With W. T. Stewart. Oxidation of alginic acid by periodic acid. J. Am. Chem. Soc., 62:1792-96.
- With David Pressman. The hydration of unsaturated compounds. VIII. The rate of hydration of beta, beta-dimethylacrylic acid; the rate of dehydration and decarboxylation of beta-hydroxy-isovaleric acid. J. Am. Chem. Soc., 62:2069-80.

- With M. J. Schlatter and R. C. Jones. The isomeric 2,3-epoxy-pentanes and 2-pentenes. The extent to which mixtures of diastereomers are formed in reactions of some pentane compounds. J. Am. Chem. Soc., 63:22-28.
- With W. Baumgarten. The reduction of tartaric acid. J. Am. Chem. Soc., 63:1653-57.
- With C. W. Gould, Jr. The conversion of the 3-chloro-2-butanols to the 2,3-dichlorobutanes; evidence for a cyclic chloronium intermediate. J. Am. Chem. Soc., 63:2541-50.

- With C. W. Gould, Jr. Brucine as a reagent for partially resolving bromoalkanes; the configuration of some diastereomeric dibromalkanes. J. Am. Chem. Soc., 64:601-3.
- With D. Pressman and L. Brewer. The hydration of unsaturated compounds. IX. The oxonium complex constant of mesityl oxide. J. Am. Chem. Soc., 64:1117-22.
- With D. Pressman and L. Brewer. The hydration of unsaturated compounds. X. The role of the oxonium complexes in the hydration of mesityl oxide and the dehydration of diacetone alcohol. J. Am. Chem. Soc., 64:1122-28.
- With D. Pressman. Hydration of unsaturated compounds. XI. Acrolein and acrylic acids. J. Am. Chem. Soc., 64:1953-57.
- With E. R. Kennedy. Diphenyliodonium iodide. Org. Syn., 22:52. With E. R. Kennedy. Iodobenzene dichloride. Org. Syn., 22:69.

- With E. R. Kennedy and M. W. Formo. Iodosobenzene. Org. Syn., 22:70.
- With E. R. Kennedy. Iodoxybenzene. I. Disproportionation of iodosobenzene. Org. Syn., 22:72.

- With R. S. Moore and D. Pressman. The coördination of silver ion with unsaturated compounds. II. cis- and trans-2-pentene. J. Am. Chem. Soc., 65:227-29.
- With F. W. Billmeyer, Jr. and D. Pressman. The coördination of silver ion with unsaturated compounds. III. Mixtures of trimethylethylene and cyclohexene. J. Am. Chem. Soc., 65:230-31.

#### 1944

With W. T. Stewart and D. Pressman. The hydration of unsaturated compounds. XII. The rate of hydration of beta, beta-dimethylacrolein and its equilibrium with beta-hydroxy-iso-valeraldehyde. J. Am. Chem. Soc., 66:1818-21.

#### 1948

With H. K. Garner. The configuration of active 2,3-epoxybutane and *erythro*-3-chloro-2-butanol. J. Am. Chem. Soc., 70:990-92.

#### 1949

With David Pressman. Principles and Practice in Organic Chemistry. New York, John Wiley & Sons, Inc.; London, Chapman & Hall, Ltd. xi + 557 pp.

# 1950

With F. W. Mitchell, Jr. and H. K. Garner. Acetolysis of the p-toluenesulfonates of the 2,3-butanediols. J. Am. Chem. Soc., 72:2138-44.

- With H. K. Garner. 1,2-dimethylethyleneiodonium ions as intermediates in reactions of the 3-iodo-2-butanols. J. Am. Chem. Soc., 72:2145-50.
- With John Michael O'Gorman. Hydrolysis of the acetal of D-(+)-2-octanol. J. Am. Chem. Soc., 72:5489-90.
- With M. S. Guthrie. Geometrical isomerism of propylene acetals. J. Am. Chem. Soc., 72:5490-91.
- With F. W. Mitchell, Jr. and C. N. Scully. Cyclic phosphites of some aliphatic glycols. J. Am. Chem. Soc., 72:5491-97.
- With H. K. Garner. Preparation and hydrolysis of some acetals and esters of D(-)2,3-butanediol. J. Am. Chem. Soc., 72:5497-5501.
  - With F.W. Mitchell, Jr. Phosphonation with a phosphite ester of propanediol. J. Am. Chem. Soc., 72:5779.

- With P. J. Leroux. L(-)-2-butanol from D(-)2,3-butanediol. J. Am. Chem. Soc., 73:41-42.
- With W. Fickett and H. K. Garner. The configuration of optically active 1,2-dichloropropane. J. Am. Chem. Soc., 73:5063-67.
- With H. Lemaire. Measurement of the basic strength of weak bases in glacial acetic acid. J. Am. Chem. Soc., 73:5198-5201.

- With F. H. Dickey and W. Fickett. Stereoisomeric 2,3-butanediamines, 3-amino-2-butanols and 2,3-dimethyl-ethyleneimines; stereochemistry of the opening and closing of the imino ring. J. Am. Chem. Soc., 74:944-51.
- With G. K. Helmcamp. Stereochemistry of the reaction of 2,3-epoxybutane with alcohols. J. Am. Chem. Soc., 74:951-54.
- With F. R. Hepner and K. N. Trueblood. Coördination of silver ion with unsaturated compounds. IV. The butenes. J. Am. Chem. Soc., 74:1333-37.
- With K. N. Trueblood. Coördination of silver ion with un-

saturated compounds. V. Ethylene and propene. J. Am. Chem. Soc., 74:1338-39.

#### 1954

- With Alan E. Comyns. The system: silver perchlorate-dioxane. J. Am. Chem. Soc., 76:1019-20.
- With Robert E. Kofahl. Coördination of polycyclic aromatic hydrocarbons with silver ion; correlation of equilibrium constants with relative carcinogenic potencies. J. Am. Chem. Soc., 76:3931-35.

#### 1955

- With R. Ghirardelli. Stereochemistry of the ring opening of 2,3-iminobutane by acetic acid. J. Am. Chem. Soc., 77:106.
- With Henry Lemaire. The mercury-catalyzed addition of acetic acid to 3-hexyne. J. Am. Chem. Soc., 77:939-46.
- With Paul Schlichta and John K. Inman. The preparation and configuration of D(-)-4,5-dimethyl-1,3-dioxolane. J. Am. Chem. Soc., 77:3784-85.

#### 1956

With W. Smith Dorsey. Coördination of silver ion with unsaturated compounds. VII. 3-hexyne. J. Am. Chem. Soc., 78:1665-69.

- With R. Ghirardelli. Stereochemistry of the opening of the imine ring with ethylamine. J. Am. Chem. Soc., 79:734-41.
- With George K. Helmkamp and Forrest L. Carter. Coördination of silver ion with unsaturated compounds. VIII. Alkynes. J. Am. Chem. Soc., 79:1306-10.
- With Alan E. Comyns. Coördination of silver ion with unsaturated

- compounds. IX. Solid complexes of silver salts with cyclohexene,  $\alpha$ -pinene and  $\beta$ -pinene. J. Am. Chem. Soc., 79:4339-41.
- With Alan E. Comyns. Coördination of silver ion and unsaturated compounds. X. Complexes of silver perchlorate and silver nitrate and alkynes. J. Am. Chem. Soc., 79:4341-44.
- With Gabriel J. Buist. Basicity constants and rates of hydration of some imines. J. Am. Chem. Soc., 79:6157-60.